

III.A.11 Reduction of Carbon Formation from Nickel Catalysts Using Nickel-Gold Surface Alloys

David L. King (Primary Contact), Yong Wang, Ya-Huei (Cathy) Chin, Robert Rozmiarek, Jianli (John) Hu

Pacific Northwest National Laboratory

P.O. Box 999

Richland, WA 99352

Phone: (509) 375-3908; Fax: (509) 375-2186; E-mail: david.king@pnl.gov

DOE Project Manager: Don Collins

Phone: (304) 285-4156; E-mail: Donald.Collins@netl.doe.gov

Objectives

- Develop methods to minimize carbon formation from nickel catalysts during hydrocarbon reformation
- Quantify effect of gold addition to nickel catalyst surface on catalyst activity and activity maintenance
- Identify role of gold in controlling nickel surface properties through surface characterization techniques
- Extend catalyst modification concepts to Ni anodes, enabling partial on-anode reforming of natural gas

Approach

- Baseline supported nickel catalyst (Ni/MgAl₂O₄) performance in reforming methane and butane
- Quantify effect of gold addition on carbon formation and reforming activity
- Develop analytical methodology to characterize nickel surface
- Verify methane reforming kinetics with Ni/YSZ (nickel/yttria-stabilized zirconia) anode
- Quantify effect of gold addition on carbon formation and reforming activity with nickel anode catalyst

Accomplishments

- Demonstrated that addition of gold to supported nickel catalyst at sub-monolayer coverage significantly retards carbon formation
- Showed that sufficient gold to retard carbon formation from nickel results in a decrease in catalyst activity of ~65-85%, and methane conversion is more affected by Au addition than butane conversion
- Determined that H₂ chemisorption provides the best method to correlate Ni availability with catalyst activity
- Identified a method based on N₂O chemisorption that may provide means to quantify step sites
- Determined that step site poisoning model does not fully explain results

Future Directions

- Obtain kinetic data for on-anode reforming to support model development
- Evaluate effect of gold addition to Ni/YSZ for methane reforming on activity and carbon formation
- Identify best methods for adding gold onto Ni/YSZ
- Evaluate effect of other additives to improve nickel anode performance (alkaline earth, Sn, Ce) as well as alloys such as Ni-Cu
- Evaluate efficacy of natural gas pre-reforming with modified Ni catalysts
- Measure activity of doped strontium titanate as sulfur-tolerant steam reforming catalyst

Introduction

The objective of this project is to determine whether alloying the surface of nickel catalysts with low concentrations of gold is an effective strategy to retard carbon formation under realistic conditions of catalyst operation for fuel reforming. The nickel-gold catalyst can be seen as a prototypical system which, when understood, could lead to alternate metal modifications of the nickel catalyst. Understanding the surface properties of the modified nickel catalyst is key to understanding and quantifying the activity and carbon resistance.

Of particular interest is the addition of gold to the nickel anode of the solid oxide fuel cell (SOFC). There is a desire to carry out on-anode reforming of natural gas directly on the anode, reducing or eliminating a pre-reformer, but carbon formation is a concern. Moreover, steam reforming on the anode is an endothermic process, and a highly active anode may develop severe temperature gradients. Therefore, reducing the activity of the anode toward steam reforming is desirable. Addition of gold to the nickel anode is attractive due to its ability to reduce carbon formation and catalyst activity.

Approach

A test reactor system was developed for steam reforming of supported nickel catalysts. The activity and activity maintenance of the catalysts in reforming both butane and methane were quantified and correlated with available nickel surface sites. The effect of addition of gold at various concentrations was also quantified in terms of activity and activity maintenance. Other tools were used to quantify the amount of carbon produced on these catalysts. Various surface analysis methods were evaluated to identify means to characterize the nickel surface, in order to both determine total available sites as well as distinguish unique sites such as step sites.

Recent research by the team has focused on quantifying the activity of the nickel SOFC anode toward methane steam reforming. This work was carried out in collaboration with core technology personnel with expertise in modeling. Our catalyst testing results will provide kinetic data for a model

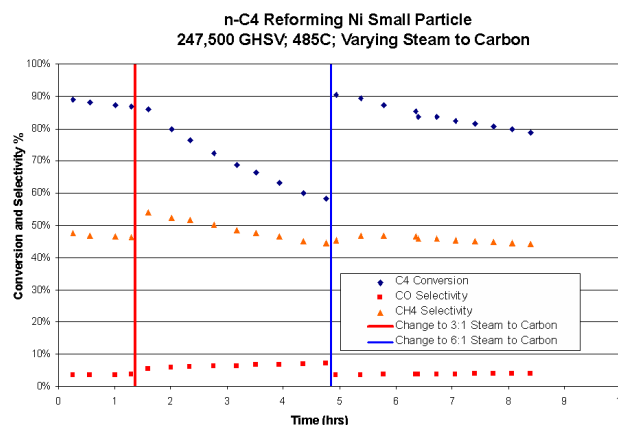


Figure 1. Supported Nickel Catalyst Shows Rapid Deactivation in Butane Reforming

that will be used to predict thermal gradients on the catalyst as a result of methane on-anode reforming using a conventional nickel anode. Significant effort was expended to make sure that the kinetic data were free of heat and mass transport limitations. This model will provide guidance regarding necessary nickel anode activity reduction in order to reduce thermal gradients across the anode surface. Research on the effect of addition of gold to the nickel anode on reduction in steam methane reforming was begun, and preliminary activity data obtained.

Results

Initial studies quantified the activity and deactivation of a supported nickel catalyst of defined crystallite size toward butane reforming at high flow rate (space velocity) and relatively low temperature. This work was done to corroborate previously published studies^{1,2} and to quantify the effect of gold addition on activity. Initial performance is shown in Figure 1, which shows activity decline at 485°C with both 6:1 and 3:1 steam:carbon (S/C) ratios. The activity could be recovered by a one-hour steam/hydrogen treatment. Figure 2 shows the effect of addition of 0.4 wt.% gold to the nickel catalyst on activity and activity maintenance. This shows clearly that the conversion was essentially stable over several hours for both 6:1 and 3:1 S/C ratios, although at lower steam content (S/C = 1.5), some decline in activity was observed. A decrease in activity by at least a factor of 3 was observed following gold addition. Figure 3 shows the effect of gold addition on steam reforming of methane over

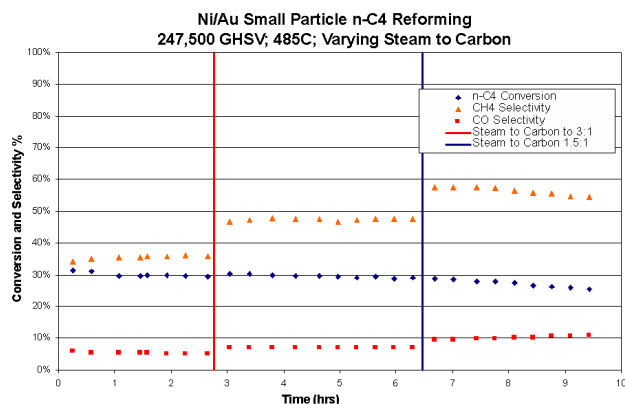


Figure 2. Addition of 0.4% Gold to Nickel Catalyst Eliminates Deactivation by Carbon Formation

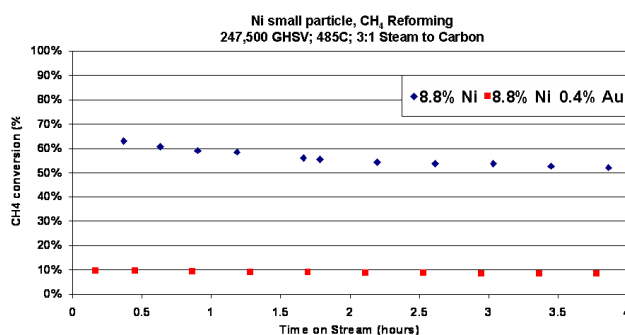
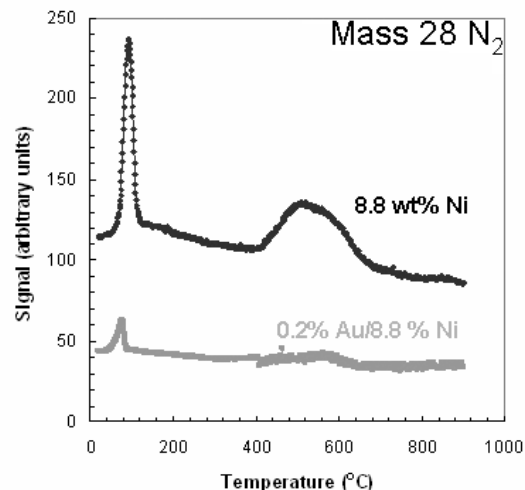


Figure 3. Effect of Gold Addition to Nickel Catalyst on Steam Reforming of Methane

this same catalyst (8.8% Ni/MgAl₂O₄). Again, addition of gold at 0.4 wt.% substantially retards deactivation on the nickel catalyst. In this case, the reduction in activity is at least a factor of 6, a greater reduction than in the case of butane.

One of the challenges in adding gold (Au) to nickel is to determine the location of gold and its form, i.e. is it on the nickel or is it simply on the support, and if on the nickel is it present as single atoms or aggregates. We used x-ray photoelectron spectroscopy (XPS) to establish the presence of Au on the surface of a 15.8 wt.% Ni/MgAl₂O₄ catalyst by showing a decrease in the nickel signal that is greater than would be expected if a bulk alloy formed or if gold were not associated with nickel. Hydrogen chemisorption measures the available surface nickel. Addition of gold drastically reduces the apparent nickel surface area, probably by altering the adsorption properties of the adjacent nickel sites by electronic effects. The decrease in activity for both



	N ₂ O	N ₂
Ni	9583	3500
Ni-Au	3430	366

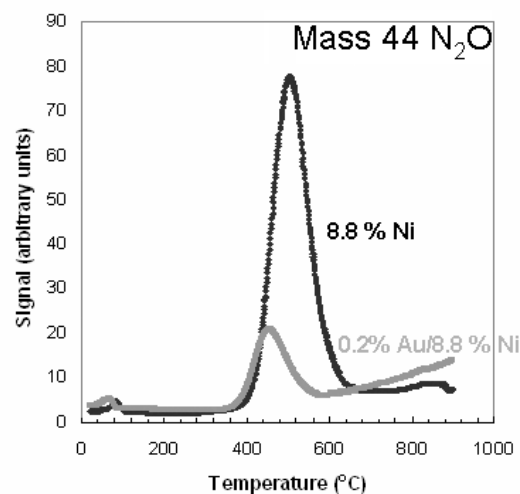


Figure 4. N₂O TPD over 8.8% Ni-0.2% Au/MgO-Al₂O₃ Catalyst

butane and methane reforming on addition of gold correlates with the decrease in hydrogen chemisorption property.

Attempts to characterize specific Ni surface sites have focused on the adsorption of nitrous oxide (N₂O) on both nickel and nickel-gold catalysts. N₂O may physically adsorb on nickel sites, or it may dissociate, with the oxygen forming a surface metal oxide site, and release nitrogen gas (N₂, mass 28). Highly active sites are expected to dissociate N₂O, whereas less active sites on nickel may simply chemisorb the N₂O molecule intact. Figure 4

compares the N_2 and N_2O signals following interaction and temperature-programmed desorption (TPD) from the surface of a 8.8 wt.% Ni/MgAl₂O₄ catalyst with and without 0.2 wt.% Au. The 8.8% Ni sample shows significant peak intensity for both N_2O and N_2 . Addition of 0.2 wt.% Au decreases both peaks, but the N_2 peak is more severely reduced, which is consistent with gold preferentially depositing on the most active nickel sites. We continue to investigate N_2O TPD as a method to characterize the nickel surface.

On-anode reforming of natural gas is a challenge, especially due to the presence of higher hydrocarbons in addition to the methane. Preliminary studies of butane reforming verified this challenge. We have observed deactivation through carbon formation even at S/C ratios as high as 6/1. The deposition of carbon on the anode is easily observed visually. Figure 5 shows that the carbon formed from reforming of butane on the Ni/YSZ anode is primarily filamentary carbon (carbon nanotubes). The bright spot in the lowermost picture, taken at 50,000 magnification with backscattering, indicated that a small particle of nickel is located at the tip of the filament. This is consistent with carbon growth proceeding from the base of the nickel particle and displacement of the particle from the surface of the anode.

Conclusions

- Carbon formation can occur with nickel-based catalysts, even when thermodynamics predict that carbon should not be formed. This is a result of competing kinetics between carbon deposition and removal.
- Addition of gold to the surface of a nickel catalyst results in significantly retarding deactivation through carbon formation, simultaneously decreasing reforming activity. The effect of gold addition on the decrease in methane steam reforming appears to be greater than the effect on higher hydrocarbon (butane) reforming.
- Hydrogen chemisorption appears to be the best method to characterize the available surface of nickel catalyst, in order to correlate surface sites with catalytic activity. This is true of both Ni and Ni/Au catalysts. Addition of gold to the nickel

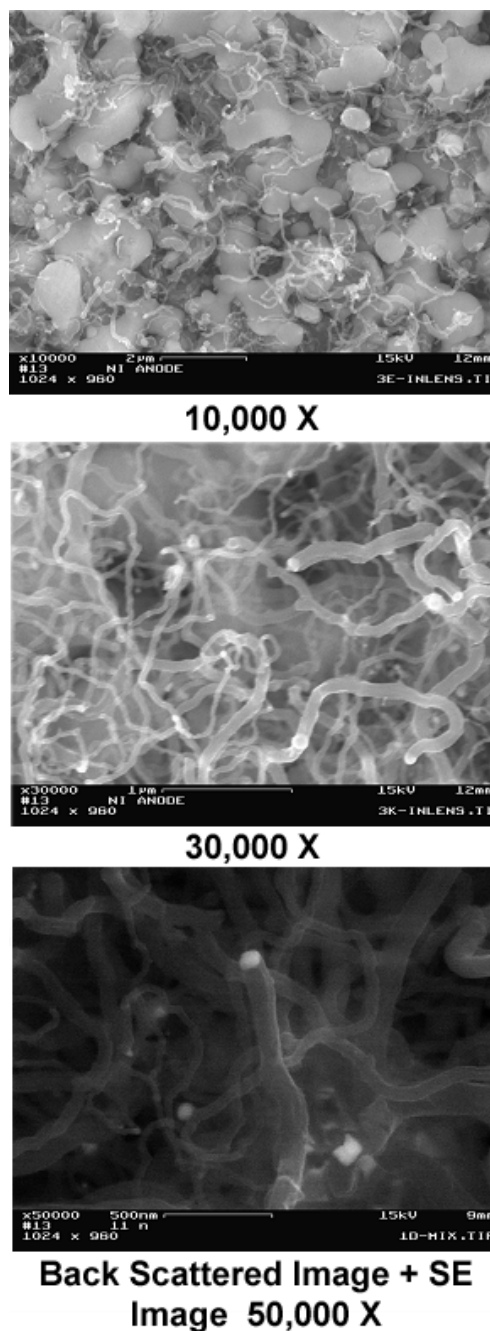


Figure 5. Scanning Electron Micrograph of Spent Ni-YSZ Anode Shows Presence of Filamentary Carbon and Evidence for Nickel at Tip of Carbon Filament

surface significantly retards chemisorption of gases such as H_2 and N_2O .

- N_2O adsorption followed by temperature-programmed desorption appears to be a promising

method to distinguish between and quantify highly active and less active Ni surface sites.

References

1. H.S. Bengaard, J.K. Norskov, J. Sehested, B.S. Clausen, L.P. Nielsen, A.M. Molenbroek, J.R. Rostrup-Nielsen; "Steam Reforming and Graphite Formation on Ni Catalysts". *J. Catalysis* 209 (2002) 365-384.
2. F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard; "Design of a Surface Alloy Catalyst for Steam Reforming". *Science* 279 (1998) 1913.

FY 2004 Publications/Presentations

1. David L. King, Yong Wang, Ya-Huei (Cathy) Chin, Robert Rozmiarek, John Hu; Reduction of Carbon Formation From Nickel Catalysts Using Nickel-Gold Surface Alloys. Presented at SECA Core Technology Program Review Meeting, Albany NY, October 1, 2003.
2. David L. King, Yong Wang, Ya-Huei (Cathy) Chin, Robert Rozmiarek, John Hu; Reduction of Carbon Formation From Nickel Catalysts Using Nickel-Gold Surface Alloys. Presented at SECA Core Technology Program Review Meeting, Boston MA, May 12, 2004.
3. Ya-Huei (Cathy) Chin, David L. King, Yong Wang, Robert Rozmiarek, John Hu; Surface Modification Of Supported Nickel Catalysts For Steam Reforming Of Hydrocarbons. Presented at the 26th Annual Symposium on Applied Surface Analysis, Pacific Northwest National Laboratory, Richland WA, June 17, 2004.